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Determination of Cyanide in Aluminum Industrial Waste Water by Ion Chromatographic and Spectrophotometric Techniques

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JOURNAL ARTICLE

Determination of Cyanide in Aluminum Industrial Waste Water by Ion Chromatographic and Spectrophotometric Techniques

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Ion chromatography, coupled with electrochemical detection, was applied in determining cyanide concentrations in the waste waters generated by the reprocessing of cathode electrodes in the aluminum industry. Ion chromatography data were compared with the results obtained from conventional spectrophotometric techniques. Common to both methods was the reflux–distillation step in which the cyanide is collected in 50 mL of 1.25 *N* sodium hydroxide solution. The ion chromatography data were found to be statistically bias high.

TABLE I: CHARACTERISTICS OF CATHODE-REPROCESSING WASTE WATER

Parameter	Average Value (mg/L) before control technologies	Average Value (mg/L) after control technologies
Total suspended solids	702	232
Fluoride	812	87.5
Nickel	0.71	1.1
Aluminum	131	15.2
Total cyanide	73.7	15.6
Iron	24	13.4
Chloride	500	—
Antimony	1.1	2.2

INTRODUCTION

A major portion of the cyanide released into the environment comes from the primary aluminum industry; specifically, from the reprocessing of cathode electrodes. It is estimated that as much as 121,000 kg (267,000 lbs) of cyanide is released by the aluminum industry each year (1). To mitigate the problem of cyanide in the environment, the Environmental Protection Agency (EPA) proposes to establish regulations on the amount of cyanide that may be released. To support the regulations, the Hazardous Waste Engineering Research Laboratory, within the EPA's Office of Research and Development, helped the Effluent Guidelines Division undertake a project to evaluate various cyanide-removal control technologies. The purpose of the field study was to evaluate the control technologies under actual operating conditions using actual waste water generated by aluminum refining. Samples were taken across each control technology as time composites and were preserved in accordance with EPA procedures (2). The samples were considered typical of aluminum waste waters and contained sizable concentrations of cyanide, suspended solids, dissolved solids, trace elements, and other components. Table I illustrates the composition of the waste waters, both before and after various cyanide-removal systems were applied.

EXPERIMENTAL

The standard EPA method for the determination of total cyanide was followed (2,3). Cyanide ion and complex cyanide were converted to hydrocyanic acid (HCN) by refluxing the sample in a mineral acid with magnesium ion present. The HCN gas was swept out of the distilling flask and carried to the absorbing solution by drawing air through the reaction vessel. The sample was removed from the scrubbing vessel and analyzed by spectrophotometry and ion chromatography. (A complete list of chemicals and apparatus necessary for refluxing and for colorimetric analysis can be found in references 2 and 3.)

For the colorimetric analysis in this study, the pyridine–barbituric acid color reagent was used, and cyanide was determined with a Perkin-Elmer (Norwalk, Connecticut) Lambda 5 UV–Vis recording spectrophotometer. A least-squares regression was fitted to the standards, and the samples were compared with the standard curve.

Ion chromatography is a new and evolving technology that combines the separation ability of ion-exchange resins with a highly specific detector, usually conductivity, to determine the concentration of individual species in multicomponent samples. The instrument used in this study was a model 2020i dual-channel ion chromatograph (Dionex, Sunnyvale, California). The detection system was a Dionex amperometric detector that responded to cyanide by interaction of a silver working electrode with a silver–silver chloride reference electrode having an applied potential of zero volts. An IC determination of cyanide was published by Rocklin and Johnson in 1983 (4) and served as the basis for the present determinations. The eluent used consisted of 14.7 m*M* ethylenediamine + 10.0 m*M* Na_2HBO_3 + 1.0 m*M* Na_2CO_3 at 3.5 mL/min (50-µL sample loop). An HPIC-AS3 anion-exchange column with an HPIC-AS3 guard column was used for the separation of the compounds.

A cyanide-standard stock solution was prepared by dissolving 2.5100 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) in distilled–deionized water and diluting to 1 L. The resulting cyanide concentration was equivalent to 1 mg of cyanide per mL of solution. The stock solution was used to prepare the working standard with a concentration of 50 µg of cyanide per

TABLE II: SUMMARY OF COLORIMETRIC AND ION CHROMATOGRAPHIC CYANIDE DATA ON ALUMINUM WASTE WATER SAMPLES*

Sample Number	Colorimetric	Ion Chromatographic	Sample Number	Colorimetric	Ion Chromatographic
1	1.39	1.00	29	2.36	2.60
2	1.20	0.38	30	3.71	3.66
3	1.05	1.00	31	12.36	11.87
4	1.00	1.00	32	4.72	5.14
5	0.84	0.85	33	1.70	2.48
6	24.86	29.76	34	6.38	6.74
7	4.20	4.40	35	3.66	3.72
8	0.89	1.14	36	4.05	3.99
9	1.79	2.18	37	4.92	5.60
10	0.80	0.79	38	4.81	5.60
11	20.17	21.75	39	9.27	10.99
12	20.20	22.38	40	4.85	5.72
13	4.46	4.21	41	4.74	5.51
14	1.98	2.25	42	9.41	9.53
15	0.70	0.75	43	17.41	17.38
16	0.22	0.30	44	17.32	17.25
17	2.20	2.36	45	17.40	17.18
18	41.08	44.60	46	16.67	17.40
19	6.99	8.40	47	0.63	0.70
20	2.76	3.20	48	0.66	0.77
21	5.53	4.69	49	14.33	16.11
22	2.57	3.30	50	16.33	17.11
23	3.06	3.32	51	16.31	17.04
24	3.12	3.40	52	0.98	0.77
25	1.75	1.78	53	9.80	9.13
26	3.45	4.30	54	0.74	0.92
27	10.57	9.46	55	0.60	0.75
28	5.07	5.35	56	5.82	6.10

* expressed in mg/L

mL. The IC detection range used for the cyanide samples was 0.05 mg/L to 0.50 mg/L, and the samples were diluted until they fell within that range. All injections into the ion chromatograph were done in duplicate and were repeated if the peak-height reproducibility was >1%. As with the colorimetric analysis, the quality control of the data was maintained by duplicate analyses, separate standards, and spiked samples.

RESULTS AND DISCUSSION

A series of industrial-waste cyanide samples was analyzed by both the EPA standard spectrophotometric method and the ion-chromatographic method. The results of the two techniques are presented in Table II. A series of cyanide standards also was analyzed by the two techniques, and the results are shown in Table III.

TABLE III: COMPARISON OF COLORIMETRIC AND ION CHROMATOGRAPHIC TECHNIQUES USING CYANIDE STANDARDS*†

Standard	Colorimetric	Ion Chromatographic
0.02	0.02	0.05
0.12	0.12	0.24
0.19	0.20	0.28
0.20	0.17	0.28
0.37	0.35	0.54
0.38	0.40	0.46
0.40	0.37	0.46
0.40	0.34	0.42
0.96	1.04	1.13
1.21	1.33	1.47

* standards having values of 0.19, 0.38, 0.96, and 0.37 mg/L cyanide are quality-control standards obtained from Environmental Monitoring and Support Laboratory, Cincinnati; the other standards listed were prepared as internal control standards

† expressed in mg/L

The data from the two techniques were compared statistically in two ways: by least squares and by percentage differences.

Least squares: (See Table IV and Figure 1.)

Percent difference: Because the spectrophotometric technique is EPA-approved, it was used as the basis for comparison. The percent difference between each data set was calculated and plotted versus colorimetric concentration (Figure 2). The comparison shows that no parabolic, linear, or exponential correlation exists. There is a definite *positive* bias of the data obtained with the IC technique, however. The concentration of cyanide determined by ion chromatography was also compared to the concentration of cyanide determined by the EPA method (335.2) (Figure 3).

It is proposed that the sodium hydroxide concentration affected the rate of cyanide elution from the column.

The bias was not recognized until after data collection was completed and statistical comparisons were made. Because of the sharp peaks for cyanide, peak-height measurement was selected as the method of measuring cyanide. The NaOH competed with cyanide ions for sites on the column, which resulted in a broader peak (relative to the standards) and thus produced biased data on the wastewater samples.

CONCLUSIONS

The determination of total cyanide (both free and strongly complexed) in cathode-reprocessing waste waters requires distillation of the sample with caustic trapping. The conventional colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L; it corresponds well with the IC results. If constant NaOH concentrations are not maintained, a positive bias in the data relative to the ion-chromatographic technique is produced.

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DISCLAIMER

Although the research described has been funded wholly or in part by the U.S. EPA, it has not been subjected to agency review and therefore does not necessarily reflect the views of the agency. No official endorsement should be inferred.

REFERENCES

(1) "Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Point Source Category, Volume

TABLE IV: STATISTICAL* COMPARISONS OF COLORIMETRY AND ION CHROMATOGRAPHY IN THE DETERMINATION OF WASTE-WATER CYANIDE CONCENTRATION

Comparison Data	*a*	*b*	r^2
Colorimetry (*y*) / Standard (*x*)	−0.039	1.113	.993
Ion chromatography (*y*) / Standard (*x*)	0.043	1.151	.988
Ion chromatography (*y*) / Colorimetry (*x*)	0.085	1.032	.990

* least-squares fit: $y = ax + b$

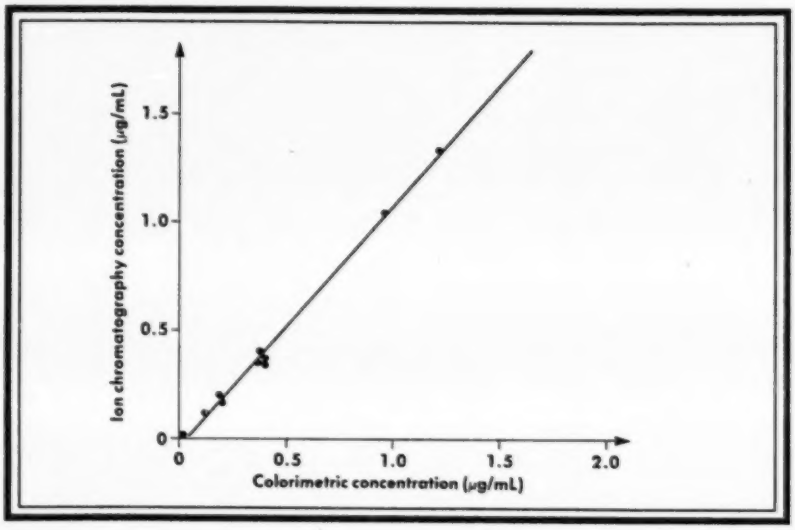

FIGURE 1: Least-squares fit of ion-chromatographic cyanide data with colorimetric data; $y = 1.032x + 0.085$, $r^2 = 0.991$ (see Table IV).

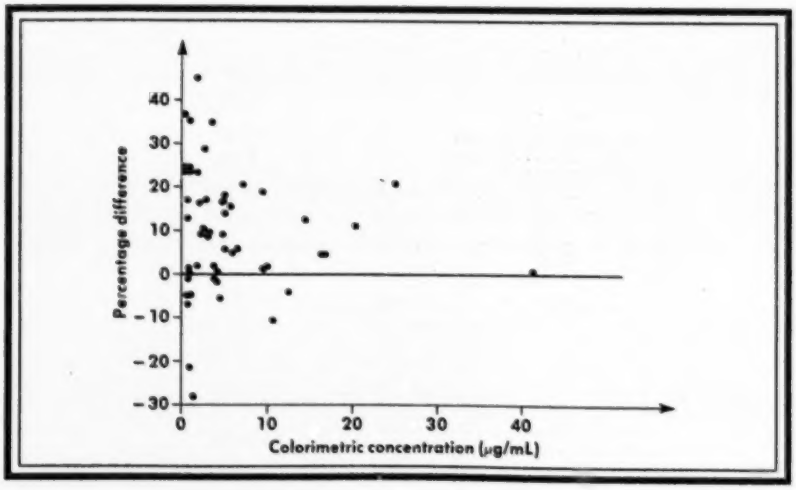

FIGURE 2: Percentage difference between colorimetric and IC techniques.

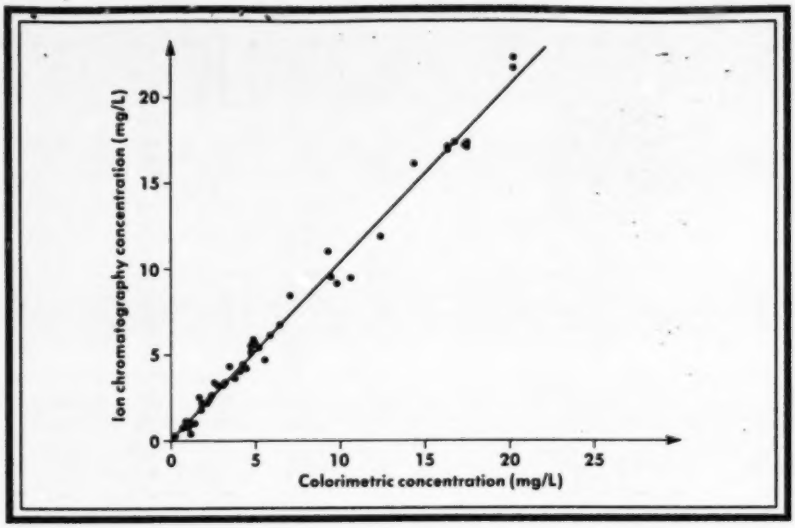

FIGURE 3: Least-squares fit of ion-chromatographic cyanide data with colorimetric data (EPA method 335.2).

II," proposed 440/1-83-019-b (U.S. EPA, Office of Water Regulations and Standards, Washington, D.C., March 1983).

(2) "Methods for Chemical Analysis of Water and Wastes" (U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 1979).

(3) "Standard Methods for the Analysis of Water and Wastewater," 15th ed. (American Public Health Association, American Water Works Association, Water Pollution Control Federation 1980).

(4) R.B. Rocklin and E.L. Johnson, *Anal. Chem.* 55, 4–7 (1983).■

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